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DOI: https://doi.org/10.1016/j.catena.2010.05.001

Originally published at:
Egli, M; Mavris, C; Mirabella, A; Giaccai, D (2010). Soil organic matter formation along a chronosequence in the Morteratsch proglacial area (Upper Engadine, Switzerland). Catena, 82(2):61 - 69.
DOI: https://doi.org/10.1016/j.catena.2010.05.001

Soil organic matter formation along a chronosequence in the Morteratsch proglacial area (Upper Engadine, Switzerland)

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Abstract

Global warming leads to the melting of ice caps and glaciers and, consequently, the exposure of new areas of land to the atmosphere and weathering. These areas usually have a high reactivity to both biotic and abiotic changes. Proglacial areas in the Alps usually have a deglaciation time span of around 150 years (time since the end of the 'Little Ice Age' in the 1850s). We investigated a chronosequence of very young soils in the proglacial area Morteratsch (Swiss Alps) to derive time-trends of soil organic matter accumulation and evolution. Total organic C and N contents, C and N contents of the various organic matter (OM) density fractions and of the labile (oxidised by H_2O_2) and stable (H_2O_2-resistant) fractions were measured. Further characterisation of OM and the various fractions was performed using Diffuse Reflection Infrared Fourier Transform (DRIFT). Soil organic matter has been accumulated over 150 yr at very high rates, values lay between 7 – 36 g C/m^2/yr. This led to a soil organic matter abundance of about 1 – 5.5 kg C/m^2 after 140 years. Even at the start of soil formation, a very stable fraction of soil organic matter was detectable. Stable organic

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Keywords: soil organic matter, proglacial area, chronosequence, density fractions, stable organic matter

1. Introduction

The rates of reactions and their dependencies on environmental factors (such as climate) are of fundamental interest to understanding the soil system and its interaction with surrounding environmental conditions. In this context, the influence of climate and time is of growing interest with respect to landscape and soil evolution because of observed and predicted global climate changes. Due to climate warming, additional areas will become ice-free and subject to weathering and soil formation. Proglacial environments are important for the understanding of global CO_2 cycling on glacial/interglacial timescales as they made up a significant amount of the global land surface during the Quaternary due to the advance and retreat of glaciers and ice sheets (Gibbs and Kump, 1994). The proglacial area is a potential zone of high geochemical reactivity due to the

availability of freshly ground reactive material (subglacially derived), high water to rock ratios and contact times, high permeability and a constant supply of diluted water (meltwaters and rain/snowmelt) percolating through the deposits (see Hosein et al., 2004; Föllmi et al., 2009). Proglacial weathering intensity depends mainly on the lithology (e.g. highly reactive minerals like carbonates and sulphates vs. crystalline rocks), the development of organic matter (Conen et al., 2007), the rate of supply of fresh rock material to the proglacial zone, the age of exposure and the character of the proglacial hydrological drainage system. Retreating glaciers successively expose mineral substrate which is colonised within a few years by soil biota, lichens and plants (Burga, 1999; Conen et al., 2007). As a consequence, soil organic matter is rapidly accumulated in proglacial areas (He and Tang, 2008). The rapid accumulation of organic C and N even accelerates the processes of soil formation (He and Tang, 2008).

Only a few studies have been done so far about the very early stages of weathering or soil formation (with ages of 0 – 150 yr). Some investigations on weakly-developed and young soils in cold environments have been carried out, among others, in the Antarctica (e.g. Kuhn, 1997; Tscherko et al., 2003; an overview is given by Beyer and Bölter, 2002). Deglaciated soils have attracted new scientific interest (Haugland, 2004; Tscherko et al., 2005; Douglass and Bockheim, 2006; Conen et al., 2007; He and Tang, 2008), because glaciers are considered to experience the greatest impacts as a result of global climate change (Goryachkin et al., 1999). Furthermore, current interest in adaptation mechanisms is also relevant to the study of deglaciated soils through the investigation of biogenic and abiogenic processes, and their interaction under extreme conditions (He and Tang, 2008).

The proglacial areas in the Alps are in most cases defined as the area between the present-day glacier and the distinct moraines deposited in the 1850s. The most evident soil changes in the Alps occur in proglacial areas where already-existing young soils are continuously developing and new soils will form due to glacier retreat (Egli et al., 2006).

The aim of our research was to study the formation of soil organic matter and its different fractions

within a time span of 0 – 150 yr. This process could be studied using a time sequence where the different glacial states and their ages are precisely known. The study of soil chronosequences is an important tool to derive short- to long-term formation rates. Studies of soil chronosequences require that soils can be differentiated on the main variable 'time' if the other factors (climate, parent material, organisms, topography) affecting soil development are subordinate or relatively constant (Jenny, 1980).

2. Materials and methods

2.1. Study area

The soils studied lie within the proglacial area of the Morteratsch glacier in the Upper Engadine (Switzerland) (Fig. 1). The border of the proglacial area is given by distinct moraines deposited in the 1850s during the 'Little Ice Age'. The actual length of this proglacial area is approx. 2 km and has an area of 1.8 km^2. The proglacial area is in a valley that runs N-S. The altitude ranges from 1900 to about 2150 m asl (Table 1). The vegetation cover of the Morteratsch proglacial area has been studied by Burga (1999). The first flowering plants colonising young deglaciated surfaces are scattered individuals of mostly sterile *Epilobium fleischeri* and *Linaria alpina* that appear after about 7 years. Epilobietum fleischeri community has a higher cover-abundance after c. 27 years. First plants of the community Oxyrietum digynae appear after c. 12 years and disappear after c. 27 years. The establishment of Larici-Pinetum cembrae forests takes place after about 77 years (Burga, 1999) on sites where the soil has more intensely developed. The glacial till consists of granite and gneissic material (Table 1). The morainic material was produced through glacial transport within a small area of relatively homogeneous parent material. Present climatic conditions for the Morteratsch site are approx. 0.5 °C mean annual temperature and approx. 1000 – 1300 mm mean annual precipitation as calculated by using data from the nearby Samedan and Bernina

meteorological stations.

2.2. Soil sampling

Soil samples were collected from 21 soil pits distributed over the whole proglacial area (Fig. 1). 10 of these sites (S1 – S10) were selected for a more detailed chemical characterisation. This procedure resulted in the collection of a soil chronosequence on surfaces with ages ranging from 0 – 150 yr. Soil profiles were excavated down to the C horizon (Table 2). For each horizon, approximately 1 – 2 kg of material was collected. Soil bulk density was measured with a soil core sampler with a known specific volume or by excavated holes with a volume of about 500 – 2000ml that were backfilled with a measurable volume of quartz sand.

2.3. Soil chemistry and physics

Total organic C and N contents of the soil (fine earth) and parent material were measured with a C/H/N analyzer (Elementar Vario EL). Soil pH (in 0.01 M $CaCl_2$) was determined on air-dried fine earth samples using a soil:solution ratio of 1:2.5.

After a pre-treatment of the samples with H_2O_2 (3%), particle size distribution of the soils was measured by a combined method consisting of sieving the coarser particles (32 – 2000 µm) and the measurement of the finer particles (< 32 µm) by means of an X-ray-sedimentometer (SediGraph 5100). The weight proportion of soil skeleton was determined by sieving the bulk soil material (2 mm sieve).

2.4. Fractionation of organic matter

Two different methods to characterise organic matter (SOM) in the topsoil were applied for the sites S1 – S10: a density fractionation and an oxidation treatment using H_2O_2.

The density fractionation procedure was adapted from Christensen (1992). The following fractions were separated: < 1 g/cm^3, 1 – 1.6 g/cm^3, 1.6 – 2.0 g/cm^3 and > 2 g/cm^3. Forty grams of fine earth

were added to 400 ml deionised water and stirred slightly. After about 12 h the sample was centrifuged for 10 min. at 5000 rpm. The supernatant was sucked off and evaporated (= density fraction < 1g/cm^3). The residual sample together with the suspended material was dried at 40°C and subjected to a sodium polytungstate solution having a density of 1.6 g/cm^3 to separate the 1 – 1.6 g/cm^3 fraction from the > 1.6g/cm^3 one. Ultrasonic treatment of the density solution was done for 40 s at 50 J/ml and it was then centrifuged for 30 minutes at 3000 rpm. In an additional step, a polytungstate solution having a density of 2.0 g/cm^3 was used to separate the 1.6-2.0 g/cm^3 from the > 2 g/cm^3 one. Ultrasonic treatment of the density solution was done for 40 s at 50 J/ml and it was then centrifuged for 30 minutes at 3000 rpm. The supernatant having floating particles (density of 1.6 to 2.0 g/cm^3) was sucked off and washed. To remove the salt, the sediment containing the associated mineral-SOM fraction with ρ > 1.6 g/cm^3 and ρ > 2.0 g/cm^3 was washed three times using distilled water. Finally, the sample was centrifuged and the supernatant was discarded. All fractions were dried at 40 °C.

Our conceptual approach was based, furthermore, on the finding that partial oxidative degradation of organic matter (OM) leaves behind intrinsically resistant as well as mineral-protected organic materials. The second method to characterise soil organic matter is based on the oxidation of OM by 10% H_2O_2 (Eusterhues et al., 2005; Plante et al., 2004, modified). 1 gram of air-dried, untreated soil (< 2mm) was wetted for 10 min with distilled water in a 150-ml beaker. Afterwards, 90 ml of 10% H_2O_2 were added. The procedure was run at a temperature of 50 °C throughout the treatment period. The beakers were closed by using two layers of parafilm to avoid evaporation of the reagent. Peroxide treatments were performed for 168h (7 days). At the end of the treatment the samples were washed three times with 40 ml deionised water and freeze-dried, their weights recorded, analysed for total C and N and organic matter functional groups using DRIFT. The amount of organic C after the H_2O_2 treatment was related to the initial content using a mass-balance approach to obtain the corresponding recoveries with

$$\text{Recovery} = (gC_{after} / gC_{before}) \times 100 \quad (1)$$

Recovery values were calculated also for nitrogen.

2.5. DRIFT measurements

Relative peak intensities were used for DRIFT analysis (Bruker, Tensor 27). Spectra were recorded from 4000 to 250 cm^{-1}. The samples were homogenised in a mill using a fine ball-mill (Zr) for 45 s (frequency 25.0). Prior to measurement, the samples were dried in the oven at 70°C.

In order to quantify the relative changes in the FT-IR spectra, we divided the values of the relative intensity (area) of each peak by the sum of the relative intensity of all the peaks taken into account and multiplied it by 100 using the software OPUS 6. For the following peak range an individual peak search and calculation of relative intensities (area) was done: (base1/base2)(cm^{-1}): 3000/2820, 1725/1710, 1660/1630, 1620/1600, 1535/1500, 1495/1470, 1470/1430, 1413/1333, 1190/1127, 1116/1050 and 1080/1030. The integration method using a linear background between the found bases (individual samples) and absorbance values was taken to calculate the relative concentration (OPUS 6). Major IR absorption bands and functional groups assignments are given in Table 3. Aliphatic compounds were calculated using the IR range 1480-1430 cm^{-1}. DRIFT measurements were performed on all density fractions, the H_2O_2 treated and untreated soil material.

Ellerbrock et al. (2009) propose to measure the A/B ratio (hydrophobicity) which indicates a relation between hydrophobic and hydrophilic groups of OM. This is done by analysing absorption bands that indicate relatively hydrophobic (3000 – 2800 cm^{-1}) and hydrophilic (1740 – 1698 and 1640 – 1600 cm^{-1}) OM functional groups.

3. Results

3.1. Soil organic matter abundance

Soils are only weakly developed and soil types within the proglacial area are predominantly Leptosols (Table 2). The Morteratsch glacier can be classified as a warm (temperate) glacier. Furthermore, the proglacial are lies below the present-day limit of permafrost (usually found at altitudes > 2400 m asl). Consequently, no permafrost is found in the proglacial area. Brief periglacial activity may, however, exist during a year. The soils have a high proportion of soil skeleton that is up to 77% of the mass. These are typical values for Alpine soils on debris or morainic substratum (Egli et al., 2001). Most soils had a loamy sand or a sandy texture and some had a sandy loam one (Table 2).

Although the weathering stage of the proglacial sites is low and max. soil age is 150 years, a distinct time-trend of soil organic carbon (SOC; whole profile) and nitrogen abundance could be observed (Fig. 2). The rather high scatter of the data with time shows that time is not the only controlling factor. The micro-topography (concavity) and the composition of the glacial till (glacier sediment transport) also exert their influence. A period of only 100 – 150 yr of soil evolution led to an accumulation of about 1 – 5.5 kg SOC/m^2 in the fine earth. It is noteworthy that the relationship of both SOC and N with age was not linear.

The time dependent sequence of the pH ($CaCl_2$) could be best described by a negative potential function. The relationship between time and pH was highly significant (Fig. 2). As soon as the parent material had been exposed to weathering, a rapid acidification started which led to a pH reduction from an initial value of about 5.5 or 6.0 to about 4.5.

3.2. Organic matter and density fractionation

The absolute concentration of C was highest in the light fractions (median values: from about 315 to 380 g C/kg). Only a weak decrease in organic C could be measured from the fraction < 1 g/cm^3 to the fraction 1.6 – 2 g/cm^3 (Fig. 3). With respect to nitrogen, no trend from the fraction < 1 g/cm^3 to the fraction 1.6 – 2 g/cm^3 was detectable. The median values varied between 14 and 17 g N/kg. Total organic carbon and nitrogen concentrations were, however, very low in the highest density

fraction (> 2 g/cm^3). Classically, the C/N ratio decreased from the light to the heavy fraction (Fig. 3). The C/N ratio of the light fraction (< 1 g/cm^3) was very high (27) which is typical for almost-undecomposed organic material. In the highest density fraction, the C/N ratio (median value) was close to 13.

At the beginning of soil formation, the largest part of soil organic carbon (SOC) was found in the light fractions (density < 1.6 g/cm^3; data not shown). After about 150 years, this fraction reduced to about 50 – 60% of the total SOC. In contrast, organic carbon in the heavy fraction (> 2 g/cm^3) steadily increased with time to about 15% of the total SOC after 150 years (Fig. 4). A similar overall trend could be observed for nitrogen. The relative proportion of N in the heavy fraction was, however, after 150 years distinctly higher than SOC. Consequently, nitrogen containing organic substances are preferentially adsorbed over C-rich organic compounds.

Funtional groups of proteic amides and consequently N rich compounds were almost not detectable with DRIFT in the fractions < 1 g/cm^3 to 1.6 – 2 g/cm^3 (Fig. 5). In the highest density fraction, however, a significant relative amount of proteic amides functional groups could be measured. This is consistent with the measured decrease of the C/N ratio with increasing density fraction and shows, again, that the highest density fraction is relatively enriched in N containing compounds.

Also the relative proportion of OH-deformation and C-O stretching of phenolic groups increased in general with increasing density. In contrast, C-O stretching of polysaccharides are definitely lower in the highest density fraction compared to the other fractions.

Humification processes can be detected by comparing the relative proportion of functional groups of the individual density fractions. A tendency towards increased humification was measurable from the low density fractions (< 1 g/cm^3) to those having a higher density (Fig. 5). Humification is defined as the transformation of macromorphological and less stable organic compounds into more stable and less biodegradable organic complexes that contribute to the formation of humus. Humification is related, for instance, to the preferential oxidation of plant polysaccharides (Fig. 5),

the formation of phenolic groups during organic matter decomposition, the selective preservation of more recalcitrant organic compounds such as lignin and others (e.g. Rosa et al., 2005).

According to Capriel (1997), the hydrophobicity index is a sensitive quantity to characterise the quality of soil organic matter. Hydrophobicity of soil organic matter is caused by methyl, methylene and methine groups present in aliphatic and aromatic (olefinic) compounds. In our study, the hydrophobicity (given by the A/B ratio) decreased significantly with increasing age (Fig. 6).

3.3. Labile and stable organic matter

The concentrations of labile and stable organic matter of the sites S1 – S10 are given in Table 4. Carbon recovery after oxidation by H_2O_2 was near 6% (median value; range: 2 – 19 %; Fig. 7) whereas for nitrogen it was 10% (range: 3 – 51%). H_2O_2 was in general very effective in removing labile organic matter. Only a weak, positive trend (not significant) of the relative proportion of resilient organic matter with time could be detected. At the very early stages of soil formation, the proportion of resilient organic matter was near 4% and increased to about 10% after about 140 years. The scatter of the data is however considerable.

The median C/N-value of the untreated soils was near 17 and after the H_2O_2 treatment about 10. Compared to the untreated soils, the H_2O_2 treatment led to a relative enrichment of nitrogen (lower C/N ratios after the treatment). The DRIFT spectra of the H_2O_2-treated samples showed that the oxidation-resistant OM was enriched in proteic amides and aromatic compounds (Fig. 8). This supports again the fact that resilient organic matter is nitrogen rich. Nonpolar compounds are composed predominantly of alkyl and aromatic functional groups, and may derive from sources such as plant waxes and cutins. Aromatic compounds may specifically interact with uncharged minerals (e.g. Kleber et al., 2007; Barbera et al., 2008). In contrast to Kleber et al. (2008) and Barbera et al. (2008), aliphatic C-H stretching was not increased.

4. Discussion

Already after 150 yr of soil formation, the soil organic matter stocks reached around 1 – 5.5 kg/m^2, which is a quite considerable amount. These values are comparable to those of He and Tang (2008) who measured a stock of 3.5 kg C/m^2 and 0.6 kg N/m^2 after 180 years of soil evolution in a proglacial area (and therefore quite similar conditions compared to Morteratsch). Also in Antarctic soils, carbon and nitrogen storage can reach very high levels already in young soils (max. a few hundred years old; 6.2 kg C/m^2 and 0.9 kg N/m^2 in the King George Islands; Beyer et al., 2002). The increase in organic matter stocks correlates with the vegetation type and cover. Conen et al. (2007) showed that vegetation cover develops quickly in proglacial areas and consequently distinct changes in the org. C content can be detected within a relatively short time span. In Alpine environments, soils developed on silicate parent material can have up to more than 40 kg organic C/m^2; with frequent values between 15 – 25 kg C/m^2 (Hitz, 2002; Egli et al., 2008). Mean annual rates of organic C accumulation during 150 yr of soil development in the proglacial area Morteratsch were in the range of 7 – 36 g C/m^2/yr. These values are even higher than rates reported from other Holocene soil chronosequences. In the Swiss Alps, Egli et al. (2001) measured accumulation rates of 6.7 – 9 g C/m^2/yr for a 400 yr sequence and 2 – 4 g C/m^2/yr for Podzols having an age of about 11000 yr. Lichter (1998) reported accumulation rates of 9g C/m^2/yr for a chronosequence developed on coastal dunes in Michigan (USA) and McPeek et al. (2007) 1 – 3 g/m^2/yr for young soils having an age of 220 – 1070 yr that developed on basalts in southern Iceland. He and Tang (2008) determined an annual organic carbon accumulation rate of 28 g/m^2 in a proglacial area with soil ages of max. 180 years. 3.5 g/m^2 per year were measured for nitrogen. Usually, organic matter accumulation in soils showed a non-linear trend tending to an asymptotic value.

The characteristics of soil organic matter also changed over the observed period. With time, more and more organic matter is transferred into the highest density fraction. Consequently, the relative proportion of the light fraction to SOM decreases. With time, SOM is better degraded and binds to

minerals. With increasing density, minerals become more important in organic matter stabilisation and also play a stronger role in determining OM composition (Sollins et al., 2009). The lightest fractions had a high C/N ratio due to the high content of plant-derived polysaccharides (Fig. 5), lignin, cutin or suberin (Sollins et al., 2006). When fractionated according to density, C and N concentration (per g fraction) and C/N ratios usually decreased with increasing particle density (Fig. 3; cf. Sollins et al., 2006; Basile-Doelsch et al., 2007). Sollins et al. (2006) showed, in an Oregon forest andic soil, that C, N and lignin phenol concentrations all decreased and ^{14}C mean residence time increased with particle density. Sollins et al. (2009) evidenced that with increasing particle density C concentration decreased, implying that the soil organic matter (OM) accumulations were thinner. With thinner accumulations they saw evidence for both an increase in ^{14}C-based mean residence time of the OM and a shift from plant to microbial origin. The evidence is based on the measured decrease in the C/N-ratio, the decrease in lignin phenols and an increase in their oxidation state. A similar tendency of decreasing C/N ratio with increasing fraction density could be also measured in the investigated soils. Furthermore, a time dependent decrease of OH-deformation and C-O stretching of phenolic groups in the highest particle density fraction occurred with increasing soils development (Fig. 9). We hypothesise that this might be due to an increasing shift from plant to microbial originated SOM (see Sollins et al., 2009).

With time humification of organic matter increases and it seems that more stable compounds are formed. This can be shown, for example, by the increase in aromatic compounds of SOM with time (Fig. 9). Aromatic compounds can indicate the presence of a more-stabilised organic matter with condensed and lignin-derived aromatic carbons (Poirer et al., 2003). Aromatic compounds have often been associated with recalcitrance. Lignin, lipids, and their derivatives have, however, often mean turnover times similar to the bulk SOM (Marschner et al., 2008). Only a small fraction of the lignin inputs seems to persist in soils and is mainly found in the fine textural size fraction (<20 µm), indicating physico-chemical stabilisation.

At the start of soil formation, organic material might not immediately or not at the same rate be

decomposed which consequently influences also the hydrophobicity of SOM. The grain size has, furthermore, a certain effect on the hydrophobicity (Capriel, 1997). Sandy soils are impoverished in hydrophilic compounds, such as carbohydrates and proteins, which is due to the lack of stabilisation through adsorption on clay and silt particles, which renders such compounds susceptible to microbial degradation and leaching. With increasing exposure time, the grain size in the proglacial soils decreased. The correlation of the skeleton and the sand content (uppermost 15 cm) with the age of the soil was negative and (weakly) significant ($p < 0.05$ and $p = 0.07$, respectively). Also the clay content showed an increasing tendency with time (although not highly significant with $p = 0.11$). The decreasing hydrophobicity of SOM in the proglacial area can be explained by the grain size effect (Capriel, 1997). The organic matter of a sandy soil usually contains more aliphatic C-H units than that in a clayey soil; and consequently sandy soils should be more hydrophobic.

Resilient organic matter (which resists to the H_2O_2 treatment) could be detected already at the start of soil formation. Around 6% of the total soil organic carbon and 10% of nitrogen were found in this fraction. These values are consistent with Favilli et al. (2008). Also in older, Alpine soils (having an age of max. 17 ky), the resilient soil organic carbon is in a range of about 10-20% and nitrogen between 8 and 50%. It is remarkable that already at a very early stage of soil formation a SOM fraction was present that was hardly oxidisable and strongly resilient. The low C/N ratio of this fraction points to its stability. With time, the relative proportion of N-H stretching of proteic amides even increased in the resilient organic matter fraction ($R^2 = 0.42$, $p = 0.03$) while the relative proportion of aromatic C=C decreased ($R^2 = 0.54$, $p = 0.01$). Aromatic compounds are either less stable and with time are degraded or expelled from the resilient fraction by other compounds (such as proteic amides). Stability of organic matter and its resistance to oxidation can be due to the capacity of the soil matrix to preserve organic matter (Theng et al., 1986; Righi et al., 1995) or to natural compound recalcitrance deriving from its biochemical characteristics, such as the presence of aliphatic macromolecules (lipids, cutans, algaenans, suberans), charcoal, sporopollenins and lignins. Kleber et al. (2007), Kögel-Knabner et al. (2008), Kleber et al. (2007) etc. showed the

importance of the mineral fraction in OM protection. According to the model proposed by Kleber et al. (2007), the formation of particularly strong organo-mineral associations appears to be favoured in the so-called "contact zone" by situations where proteinaceous materials unfold upon adsorption.

5. Conclusions

We studied organic matter evolution in very young soils (having a maximum age of 140 years) of a high Alpine proglacial area and made the following principal findings:

- The accumulation rate of soil organic matter was rapid with 7 – 36 g C/m^2/yr. This led to a soil organic matter abundance, after 140 years, in the range of 1 – 5.5 kg C/m^2. Such rates are high and demonstrate the reactivity of young landscapes surfaces to changing environmental conditions.
- At the start of soil formation, a very high proportion of soil organic matter was found in the fractions < 1.6 g/cm^3. After about 140 years, 15% of the soil organic carbon and 35 – 40% of the nitrogen were found in the highest density fraction (> 2 g/cm^3).
- Classically, the C/N ratio decreased from the light to the densest fraction. The C/N ratio of the light fraction (< 1 g/cm^3) was very high (27), which is typical for organic material that has suffered almost no decomposition. In the highest density fraction, the C/N ratio (median value) was close to 13.
- Stable organic matter (resistant to the H_2O_2 treatment) could be found in the soils from the start of their formation. About 6 % of the soil organic carbon and 10% of the nitrogen was found in this fraction.
- The stable organic matter, similar to the highest density fraction, was characterised by a low C/N ratio. This demonstrates a strong interaction with the mineral part of the soil. Proteinaceous material was enriched in the stable OM as well as in the highest density fraction.

Acknowledgements

This research was partially supported by the Swiss National Foundation (SNF), project grant n. 200021-117568. We would like to thank B. Kägi for the support in the laboratory. We are, furthermore, indebted to Hans-Peter Blume and an unknown reviewer for their helpful comments on an earlier version of the manuscript.

References

Barbera, V., Raimondi, S., Egli, M., Plötze, M., 2008. The influence of weathering processes on labile and stable organic matter in Mediterranean volcanic soils. Geoderma 143, 191-205.

Basile-Doelsch, I., Amundson, R., Stone, W.E.E., Borschneck, D., Bottero, J.Y., Moustier, S., Masin, F., Colin, F., 2007. Mineral control of carbon pools in a volcanic soil horizon. Geoderma 137, 477-489.

Beyer, L., Bölter, M. (eds.), 2002. Geoecology of Antarctic ice-free coastal landscapes. Ecological Stud. 154. Springer, Berlin.

Beyer, L., White, D.M., Blume, H.-P., Bölter, M., Kuhn, D., Pingpank, K., Vogt, B., 2002. Refractory soil organic matter – formation, accumulation, translocation and transformation. In: Beyer, L., Bölter, M. (Eds.), Geoecology of Antarctic ice-free coastal landscapes. Ecological Studies 154, Springer Verlag, Berlin, pp. 139-159.

Burga, C., 1999. Vegetation development on the glacier forefield Morteratsch (Switzerland). Applied Vegetation Science 2, 17-24.

Capriel, P., 1997. Hydrophobicity of organic matter in arable soils: influence of management. European Journal of Soil Sciience 48, 457-462.

Christensen, B.T., 1992. Physical fractionation of soil and organic matter in primary particle size

and density separates. Advances in Agronomy 20, 1–90.

Conen, F., Yakutin, M.V., Zumbrunn, T., Leifeld, J., 2007. Organic carbon and microbial biomass in two soil development chronosequences following glacial retreat, European Journal of Soil Science 58, 758-762.

Douglass, D.C., Bockheim, J.G., 2006. Soil-forming rates and processes on Quaternary moraines near Lago Buenos Aries, Argentina. Quaternary Research 65, 293–307.

Egli, M., Fitze, P., Mirabella, A., 2001. Weathering and evolution of soils formed on granitic, glacial deposits: results from chronosequence of Swiss alpine environments. Catena 45, 19-47.

Egli, M., Wernli, M., Kneisel, C., Haeberli, W., 2006. Melting glaciers and soil development in the proglacial area Morteratsch (Swiss Alps): I Soil type chronosequence. Arctic, Antarctic, and Alpine Research 38, 499-509.

Egli, M., Merkli, C., Sartori, G., Mirabella, A., Plötze, M., 2008. Weathering, mineralogical evolution and soil organic matter along a Holocene soil toposequence on carbonate-rich materials. Geomorphology 97, 675-696.

Ellerbrock , R.H., Gerke, H.H., Böhm, C., 2009. In situ DRIFT characterization of organic matter composition on soil structural surfaces. Soil Science of America Journal 73, 531-540.

Eusterhues, K., Rumpel, C., Kögel-Knabner, I., 2005. Stabilization of soil organic matter isolated via oxidative degradation. Organic Geochemistry 36, 1567-1575.

Favilli, F., Egli, M., Cherubini, P., Sartori, G., Haeberli, W., Delbos, E. 2008. Comparison of different methods of obtaining a resilient organic matter fraction in Alpine soils. Geoderma 145, 355-369.

Föllmi, K.B., Arn, K., Hosein, R., Adatte, T., Steinmann, P., 2009. Biogeochemical weathering in sedimentary chronosequences of the Rhône and Oberaar Glaciers (Swiss Alps): Rates and mechanisms of biotite weathering. Geoderma 151, 270-281.

Gibbs M. T., Kump L. R., 1994. Global chemical erosion during the last glacial maximum and the present: Sensitivity to changes in lithology and hydrology. Paleoceanography 9, 529–543.

Goryachkin, S.V., Karavaeva, N.A., Targulian, V.O., Glazov, M.V., 1999. Arctic soils: spatial distribution, zonality and transformation due to global change. Permafrost and Periglacial Processes 10, 235–250.

Guo, Y., Bustin, R.M., 1997. Micro-FTIR spectroscopy of liptinite macerals in coal. International Journal of Coal Geology 36, 259-275.

Haugland, J. E., 2004. Formation of patterned ground and fine-scale soil development within two late Holocene glacial chronosequences: Jotunheimen, Norway. Geomophology 61, 287 – 301.

He, L., Tang, Y., 2008. Soil development along primary succession sequences on moraines of Hailuogou Glacier, Gongga Mountain, Sichuan, China. Catena 72, 259-269.

Hitz, C., 2002. Inventur und Dynamik der organischen Substanz in Böden der alpinen Stufe. Schriftenreihe Physische Geographie, 42, Universität Zürich.

Hosein, R., Arn, K., Steinmann, P., Adatte, T., Föllmi, K. B., 2004. Carbonate and silicate weathering in two presently glaciated, crystalline catchments in the Swiss Alps. Geochimica et Cosmochimica Acta 68, 1021-1033.

Jenny, H., 1980. The soil resource. Springer, New York.

Kleber, M., Sollins, P., Sutton, R., 2007. A conceptual model of organo-mineral interactions in soils: self-assembly of organic molecular fragments into zonal structures on mineral surfaces. Biogeochemistry 85 1, 9-24.

Kögel-Knabner, I., Guggenberger, G., Kleber, M., Kandeler, E., Kalbitz, K., Scheu, S., Eusterhues, K., Leinweber, P., 2008. Organo-mineral associations in temperate soils: Integrating biology, mineralogy, and organic matter chemistry. Journal of Plant Nutrition and Soil Science 171, 61-82.

Kuhn, D., 1997. Genese, Ökologie und Soziologie einer Bodengesellschaft in einem Periglazialgebiet der King-George-Insel (West-Antarktis). Schriftenreihe Institut für Pflanzenernährung und Bodenkunde Universität Kiel, 40, 1 – 173.

Lichter, J., 1998. Rates of weathering and chemical depletion in soils across a chronosequence of Lake Michigan sand dunes. Geoderma 85, 255-282.

Marschner, B., Brodowski, S., Dreves, A., Gleixner, G., Gude, A., Grootes, P.M., Hamer, U., Heim, A., Jandl, G., Ji, R., Kaiser, K., Kalbitz, K., Kramer, C., Leinweber, P., Rethemeyer, J., Schäffer, A., Schmidt, M.W.I., Schwark, L., Wiesenberg, G.L.B., 2008. How relevant is recalcitrance fort the stabilization of organic matter in soils? Journal of Plant Nutrition and Soil Science 171, 91-110.

McPeek, T., Wang, X.Z., Brown, K., Filipelli, G.M., 2007. Rates of carbon ingrowth and nutrient release from young Icelandic basalts. JOKULL 57, 37-44.

Piccolo, A., Mirabella, A., 1985. Effetto di differenti estraenti inorganici e organici su alcune proprietà chimiche e chimico-fisiche di un acido umico. Annali dell'Istituto Sperimentale per lo Studio e Difesa Suolo XVI, 159-168.

Plante, A.F., Chenu, C., Balabane, M., Mariotti, A., Righi, D., 2004. Peroxide oxidation of clay-associated organic matter in a cultivation chronosequence. European Journal of Soil Science 55, 471-478.

Righi, D., Dinel, H., Shulten, H.R., Schnitzer, M., 1995. Characterization of clay-organic matter complexes to oxidation by peroxide. European Journal of Soil Science 46, 423-429.

Rosa, A.H., Simões, M.L., de Oliviera, L.C., Rocha, J.C., Neto, L.M., Milori, D.M.B.P., 2005. Multimethod study of the degree of humification of humic substances extracted from different tropical soil profiles in Brazil's Amazonian region. Geoderma 127, 1-10.

Senesi, N., V. D'Orazio, G. Ricca, 2003. Humic acids in the first generation of EUROSOILS. Geoderma 116, 325-344.

Sollins, P., Swanston, C., Kleber, M., Filley, T., Kramer, M., Crow, S., Caldwell, B.A., Lajtha, K., Bowden, R., 2006. Organic C and N stabilization in a forest soil: Evidence from sequential density fractionation. Soil Biology & Biochemistry 38, 3313-3324.

Sollins, P., Kramer, M.G., Swanston, C., Lajtha, K., Filley, T., Aufdenkampe, A.K., Wagai, R., Bowden, R.D., 2009. Sequential density fractionation across soils of contrasting mineralogy: evidence for both microbial- and mineral-controlled soil organic matter stabilization. Biogeochemistry 96, 209-231.

Stevenson, F.J., 1994. Humus chemistry: genesis, composition, reactions. 2nd ed., Wiley, New York.

Tan, K. H., 2003. Humic Matter in Soil and the Environment. Marcel Dekker, Inc., New York.

Theng, B.K.G., Churchman, G.J., Newman, R.H., 1986. The occurrence of interlayer clay-organic complexes in two New Zeland soils. Soil Science 142, 262-266.

Tscherko, D., Bölter, M., Beyer, L., Chen, J., Elster, J., Kandeler, E., Kuhn, D., Blume, H.-P., 2003. Biomass and enzyme activity of two soil transects at King George Island, Maritime Antartica. Arctic, Antarctic and Alpine Research 35, 34-47

Tscherko, D., Hammesfahr, U., Zeltner, G., Kandeler, E., Böcker, R., 2005. Plant succession and rhizosphere microbial communities in a recently deglaciated alpine terrain. Basic and Applied Ecology 6, 367-383.

Table 1. General features of the Morteratsch proglacial area

Latitude	46°26'N
Longitude	9°56'E
Elevation at glacier front	2117 m asl
Elevation at pro-glacial area front	1900 m asl
Main orientation	North
Geology	Granite and granodiorite
Mean annual temperature	0.5 °C
Mean annual precipitation	1100 – 1300 mm
Mean slope	<10°

Table 2
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Table 2. Some physical and chemical properties of the investigated soils.

Site/Soil unit (FAO, 1998)	Soil age (yr)	Horizons	Depth (cm)	Bulk density (g/cm^3)	Skeleton (wt. - %)	Sand (g/kg)	Silt (g/kg)	Clay (g/kg)	pH ($CaCl_2$)	Org. C (g/kg)
S1/Humi-Skeletic Leptosol	138	O	0-6	0.2	41	n.m.*	n.m.	n.m.	4.60	321.1
		A	6-9	1.6	50	777	184	39	4.80	6.2
		BC	9-14	1.6	53	830	158	12	4.70	3.7
		C	14-30	1.8	40	757	222	21	4.60	2.8
S2/Humi-Skeletic Leptosol	128	A	0-10	1.4	64	754	204	42	4.85	13.8
		AC	10-40	1.5	68	695	272	33	4.90	4.8
S3/Humi-Skeletic Leptosol	108	A	0-3	1.1	54	667	265	68	5.10	28.1
		AC	3-15	1.7	70	677	281	42	4.50	3.9
S4/Humi-Skeletic Leptosol	98	A	0-1	0.8	55	n.m.	n.m.	n.m.	5.30	56.0
		AC	1-5	1.7	51	939	61	15	5.20	4.2
		C	5-30	1.6	70	931	57	12	5.20	1.8
S5/Humi-Skeletic Leptosol	68	A1	0-1	0.8	7	n.m.	n.m.	n.m.	4.85	40.3
		A2	1-4	1.5	1	530	432	38	4.55	5.0
		C1	4-9	1.4	36	573	387	40	4.65	2.5
		C2	9-20	1.8	64	570	372	58	4.60	3.7
S6/Skeletic Leptosol	48	A	0-2.5	1.6	64	n.m.	n.m.	n.m.	4.80	37.5
		C	2.5-25	1.7	68	852	129	19	5.00	2.1

S7/Skeletic Leptosol	48	A	0-4	1.4	26	n.m.	n.m.	n.m.	6.10	60.2
		C1	4-11	1.6	37	823	146	31	5.20	2.8
		C2	11-34	2	67	747	211	42	5.10	3.7
S8/Skeletic Leptosol	58	OA	0-12	1	63	n.m.	n.m.	n.m.	4.60	118.2
		C	12-33	1.8	48	712	220	68	4.40	3.1
S9/Humi-Skeletic Leptosol	73	O	0-3	0.5	44	n.m.	n.m.	n.m.	5.15	147.8
		AC	3-10	1.5	65	785	175	40	4.40	4.8
		C	10-36	1.7	58	832	133	35	4.65	3.3
S10/Humi-Skeletic Leptosol	78	A1	0-2	0.6	49	n.m.	n.m.	n.m.	4.70	53.4
		A2	2-10	1.7	68	818	143	39	4.50	5.2
		AC	10-25	1.7	84	733	219	48	4.80	4.3
A/Humi-Skeletic Leptosol	140	A	0-7	1.4	65	770	190	40	5.20	34.3
		(Bw)A	7-25	1.9	59	780	190	30	5.10	3.7
		C	>25	1.9	64	780	190	30	5.40	2.5
1/Skeletic Fluvisol	140	(C)A	0-2	1	11	550	360	90	4.80	16.4
		(C)A	2-8	1	11	550	360	90	4.80	16.4
		2C	8-14	1.3	19	490	420	90	4.90	8.4
		3C	14-23		70	n.m.	n.m.	n.m.	4.90	8.4

2/Humi-Skeletic Leptosol	120	A	0-3	1.5	40	754	204	42	5.50	176.1
		C	3-13	1.5	65	695	272	33	4.90	16.7
3/Skeletic Leptosol	100	A	0-2	1.5	40	667	265	68	n.m.	6.9
		C	2-26	1.5	70	677	281	42	5.00	1.7
4/Skeletic Leptosol	80	A	0-2	1.1	15	n.m.	n.m.	n.m.	n.m.	5.2
		AC	2-6	1.5	70	850	120	30	4.50	5.2
		(B)C	6-8	1.5	75	850	120	30	4.50	5.2
		C	8-14	1.4	75	840	140	20	4.80	1.7
5/Skeletic Leptosol	70	A	0-3		40	818	143	39	n.m.	n.m.
		C	3-22	1.3	68	730	220	50	4.50	4.4
6/Skeletic Leptosol	60	CA	0-12	1.5	55	850	130	20	5.10	6.0
7/Skeletic Leptosol	30	AC	0-6	1.5	53	920	60	20	5.20	1.9
		C	6-25	1.4	70	830	140	30	5.40	0.7
8/Skeletic Leptosol	30	(A)C	0-15	1.6	66	820	170	10	5.70	2.0
9/Skeletic Leptosol	20	(A)C	0-18	1.8	77	n.m.	n.m.	n.m.	5.70	2.0

10/Lithic Leptosol	10	C	0-9	1.7	75	750	220	30	5.80	0.9

* n.m. = not measured

Table 3. Major IR absorption bands and assignments (Piccolo and Mirabella, 1985; Stevenson, 1994; Guo and Bustin, 1997; Senesi et al., 2003; Tan, 2003).

Band	Wave number cm^{-1}	Assignment
1	2980-2880	Aliphatic C-H stretching (aliphatic methyl and methylene groups)
2	1725-1710	C=O stretching of COOH, aldehydes and ketones
3	1660-1630	C=O stretching of amide groups, quinone C=O and/or C=O of H-bonded conjugated ketones
4	1620-1600	Aromatic C=C, strongly H-bonded C=O of conjugated ketones
5	1535-1500	Aromatic rings, amide II vibrations
6	1495-1470	N-H stretching of proteic amides
7	1470-1440	Aliphatic C-H stretching
8	1413-1333	OH deformation and C-O stretching of phenolic groups
9	1190-1127	C-OH stretching of aliphatic, alcoholic O-H
10	1116-1050	Secondary alcohols
11	1080-1030	C-O stretching of polysaccharide

Table 4. Stable (resistant to the H_2O_2 treatment) and labile organic matter in the topsoil of the investigated sites.

Site	Horizon	Stable OM fraction			Labile OM fraction		
		C (g/kg)	N (g/kg)	C/N	C (g/kg)	N (g/kg)	C/N
S1	A	1.2	0.14	8.3	5.0	0.18	27.9
S2	A	0.8	0.09	9.2	12.9	0.67	19.3
S3	A	1.5	0.25	6.0	26.6	1.33	20.0
S4	A	3.5	0.25	14.2	52.5	2.85	18.4
S5	A1	0.9	0.10	8.6	39.4	1.24	31.8
S6	A	3.4	0.22	15.3	34.1	1.47	23.2
S7	A	6.2	0.31	20.1	54.0	4.89	11.0
S8	OA	5.3	0.47	11.4	112.9	5.85	19.3
S9	O	7.1	0.33	21.5	140.7	8.63	16.3
S9	AC	0.3	0.07	4.9	4.5	0.23	19.4
S10	A1	1.9	0.18	10.8	51.5	2.55	20.2
S10	A2	0.5	0.12	4.0	4.7	0.11	42.5

Figure captions

Fig. 1. Location of the Morteratsch proglacial area (Engadine, SE Switzerland) and sampling sites within the proglacial area. The retreat phases of the glacier (isochrones) are according to Burga (1999).

Fig. 2. Soil chemical properties within the proglacial area as a function of time. The soil pH refers to the topsoil (uppermost 15cm). Organic C and N are given as stocks (kg/m^2).

Fig. 3. Box plots (median, 25th- and 75th-percentile values, min. and max. values) of organic C (A) and N (B) concentrations and C/N ratio (C) in the different density fractions.

Fig. 4. Relative amount (amount stored in the fraction of interested divided by the total amount (including all fractions: < 1 g/cm^3, $1 – 1.6$ g/cm^3, $1.6 – 2$ g/cm^3, > 2 g/cm^3)) of org. C and N in the fraction > 2 g/cm^3 of the surface horizons as a function of the soil age.

Fig. 5. Box plots (median, 25th- and 75th-percentile values, min. and max. values) of the relative proportion of, A) N-H stretching of proteic amides, B) OH deformation and C-O stretching of phenolic groups and C) C-O stretching of polysaccharide in the density fractions < 1 g/cm^3, $1 – 1.6$ g/cm^3, $1.6 – 2$ g/cm^3 and > 2 g/cm^3.

Fig. 6. Temporal evolution of the hydrophobicity (A/B-ratio) of soil organic matter in the surface horizons. The hydrophobicity is calculated using the ratio of the relative amount of hydrophobic ($3000 – 2800$ cm^{-1}) to hydrophilic ($1740 – 1698$ and $1640 – 1600$ cm^{-1}) OM functional groups.

Fig. 7. Box plots (median, 25th- and 75th-percentile values, min. and max. values) of the relative proportion of (A) the stable C and N (not oxidised by the H_2O_2 treatment) and of (B) the C/N ratio in the untreated and treated (H_2O_2) samples.

Fig. 8. Box plots (median, 25th- and 75th-percentile values, min. and max. values) of the relative proportion of aromatic C=C and N-H stretching of proteic amides before and after the H_2O_2 treatment.

Fig. 9. Temporal evolution of A) OH deformation and C-O stretching of phenolic groups in the fractions < 1 g/cm^3, 1 – 1.6 g/cm^3, 1.6 – 2 g/cm^3 and > 2 g/cm^3 of the surface horizons and B) aromatic compounds in the bulk soil OM.

Figure 1

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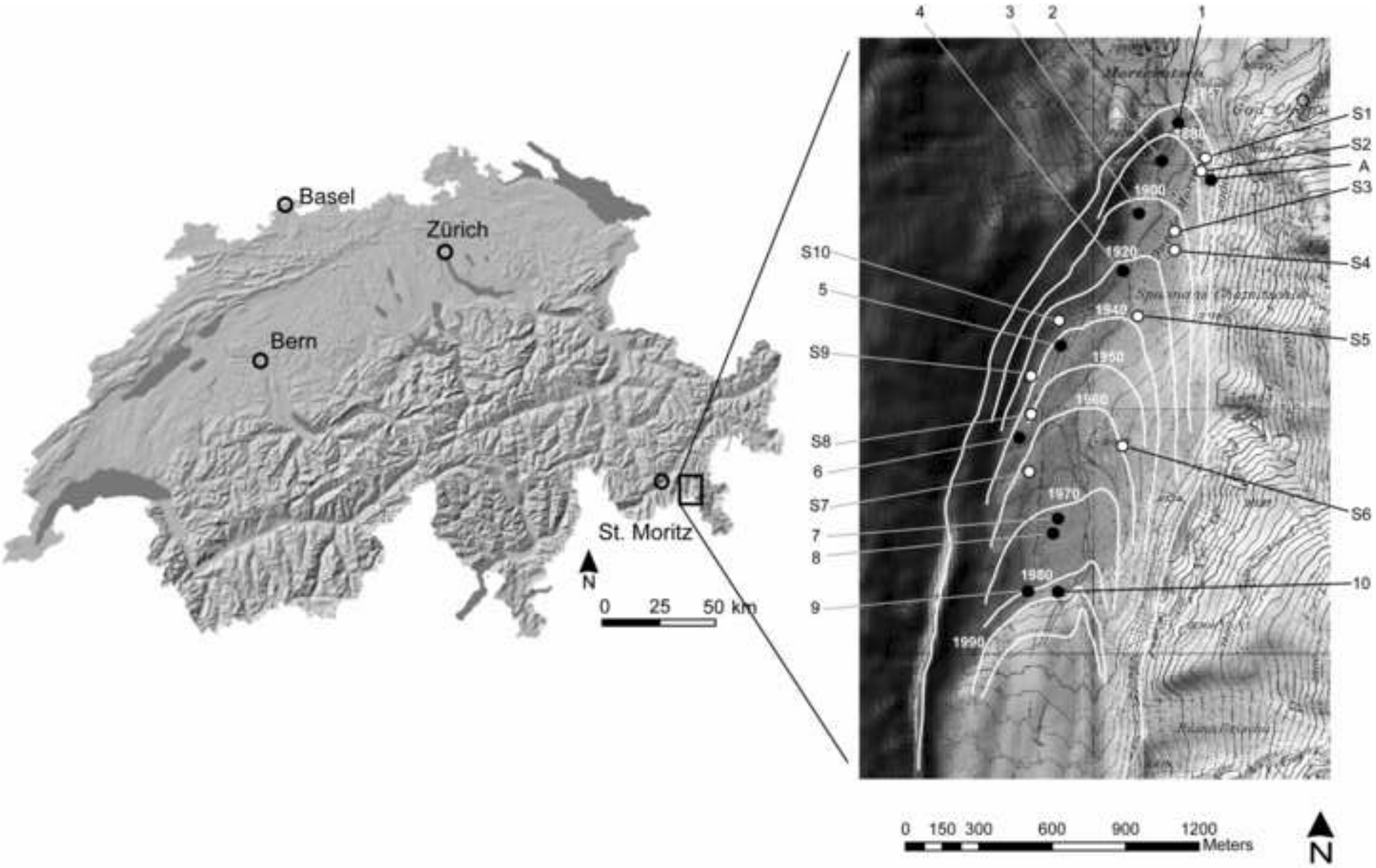

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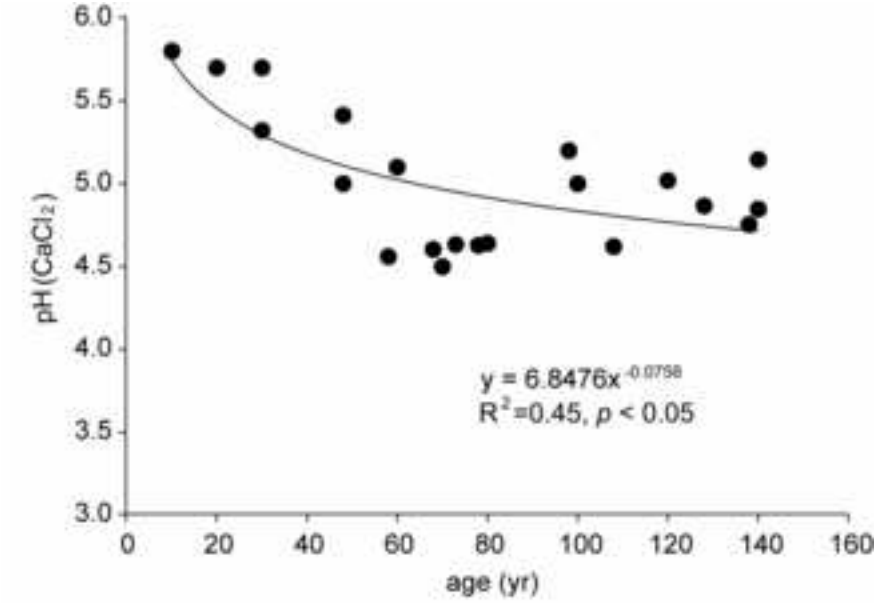

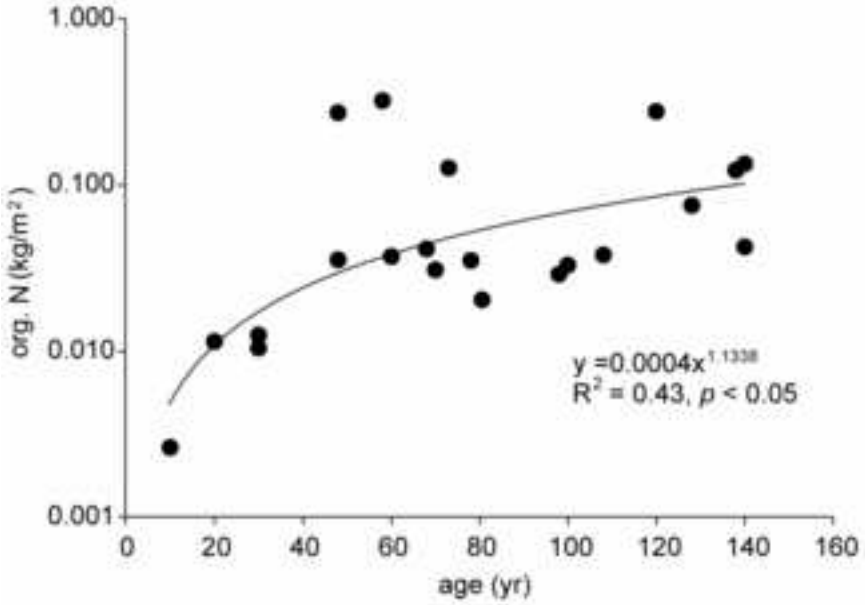

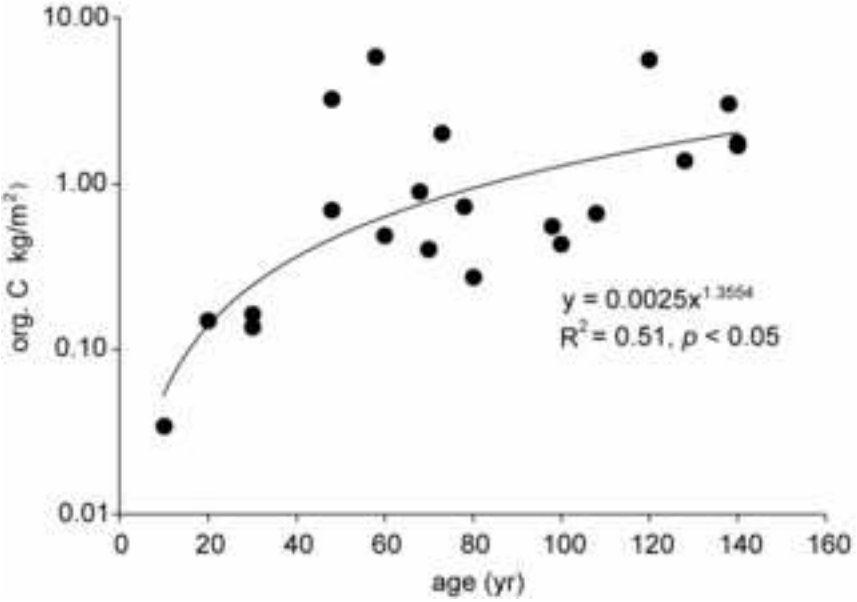

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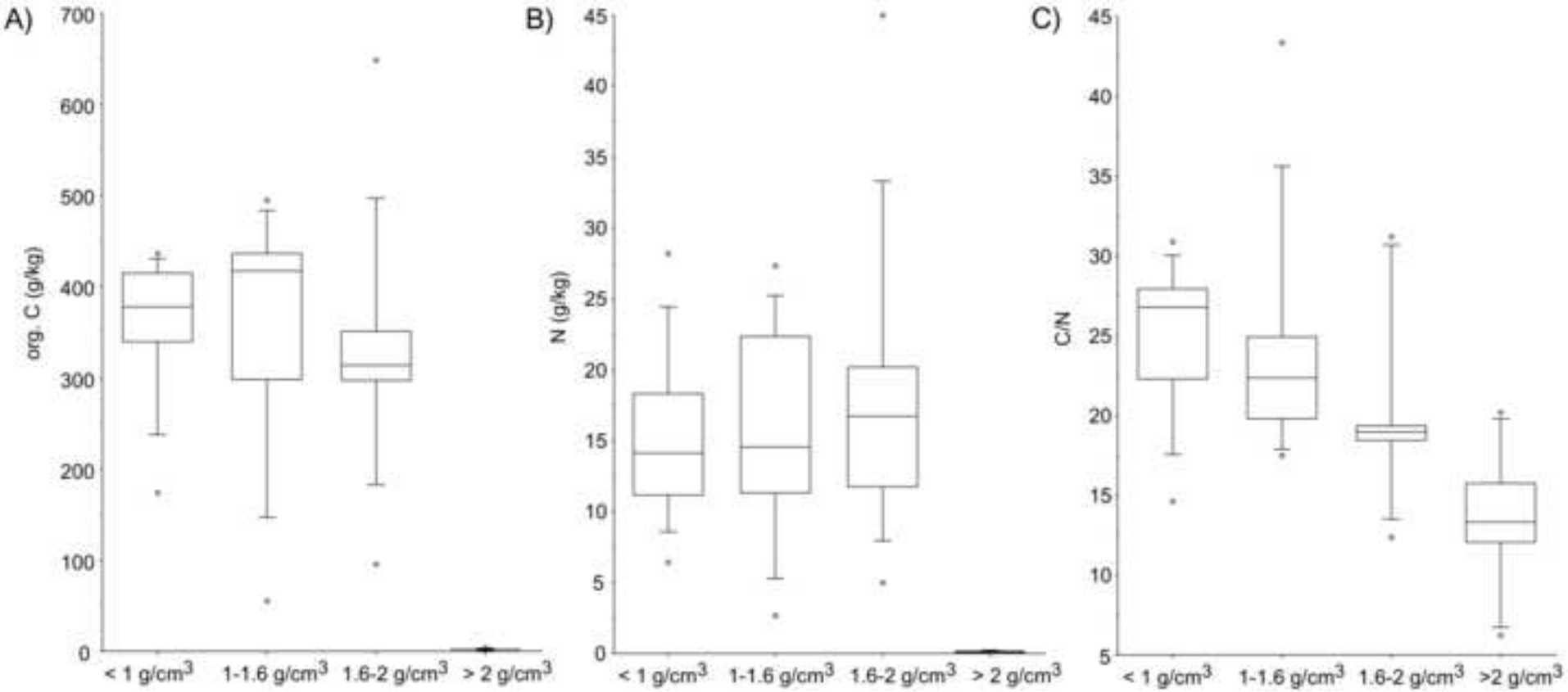

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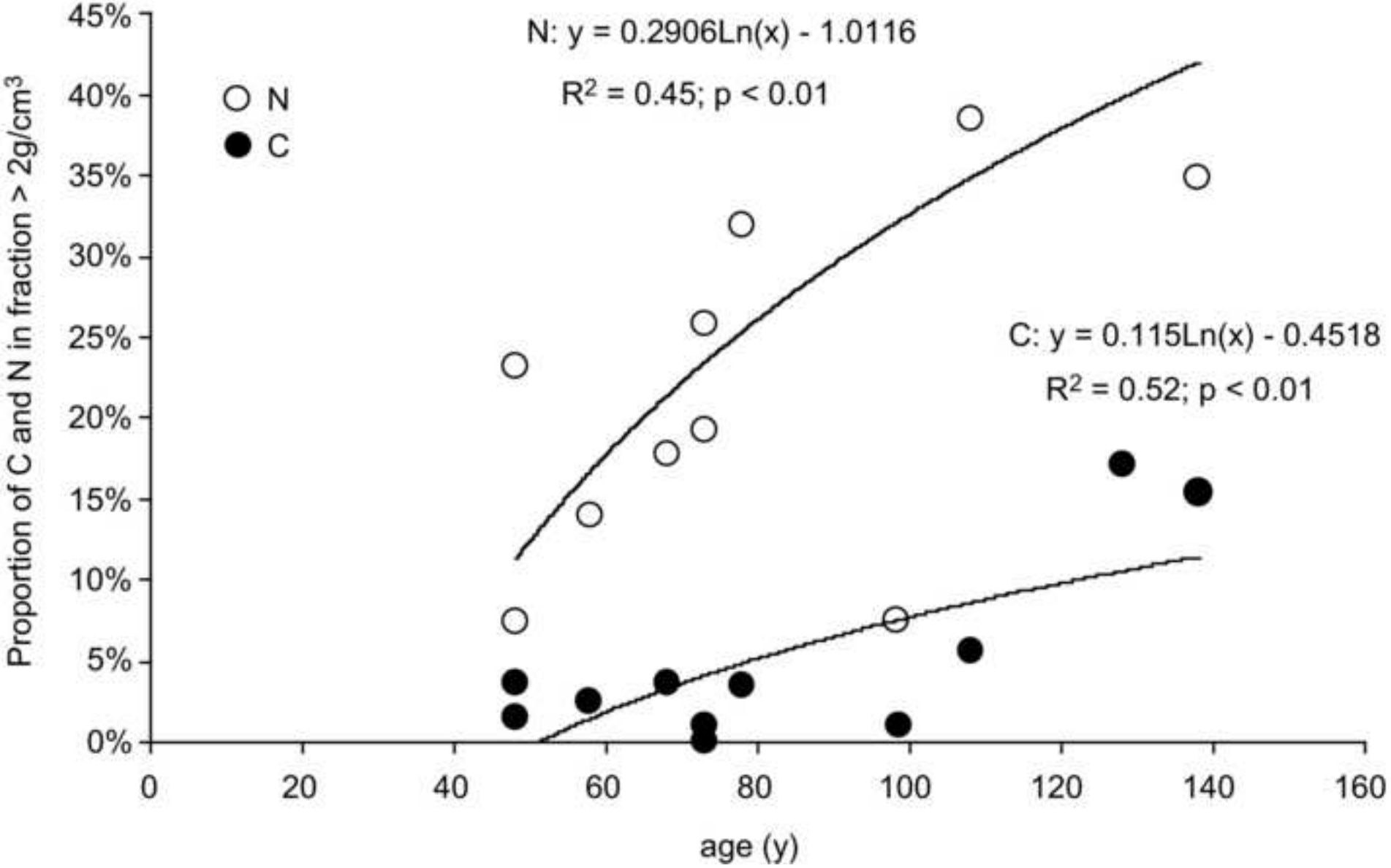

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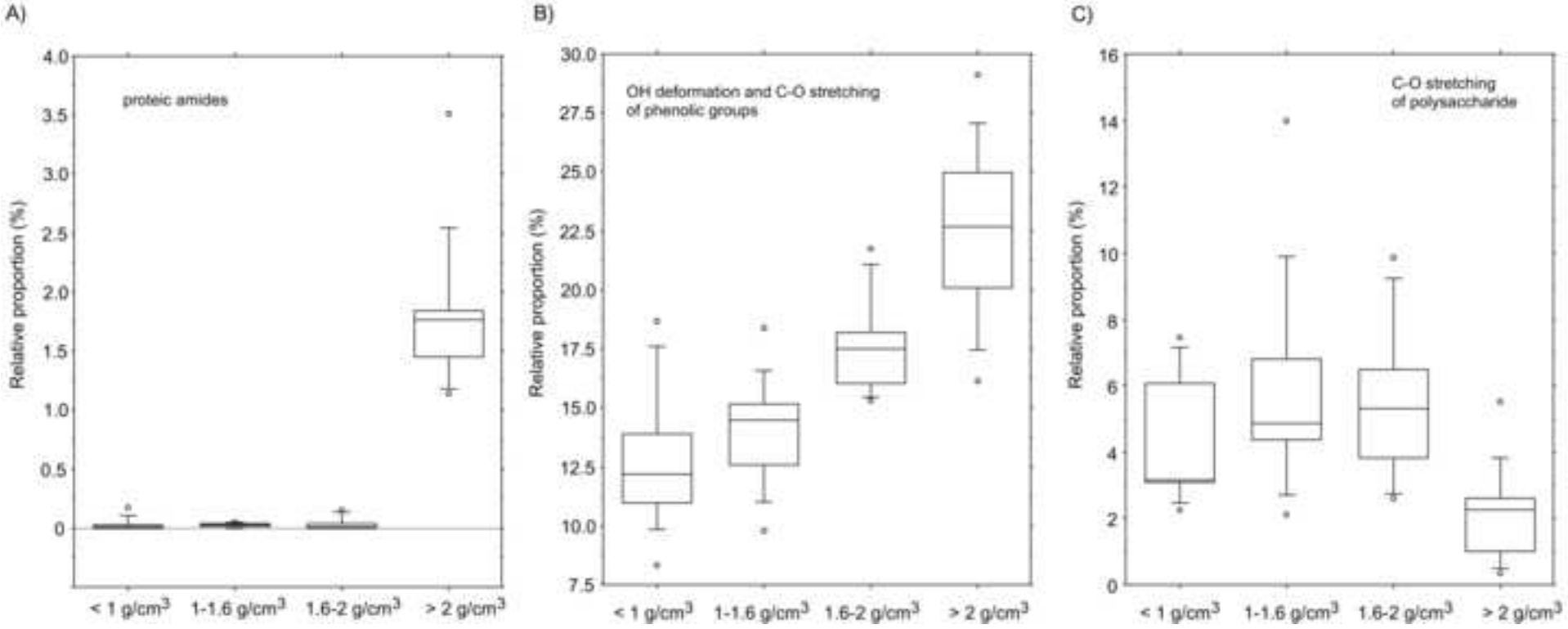

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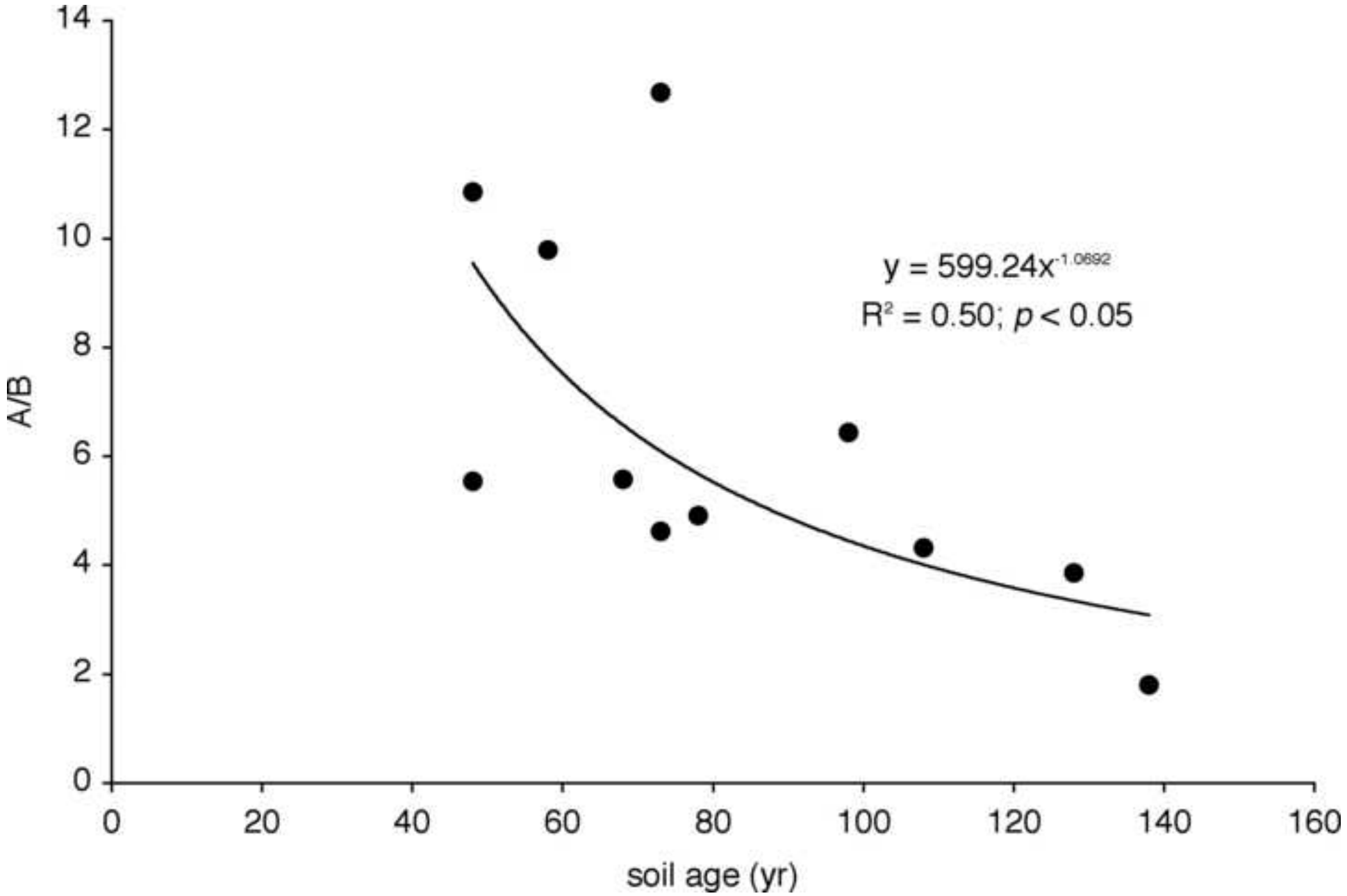

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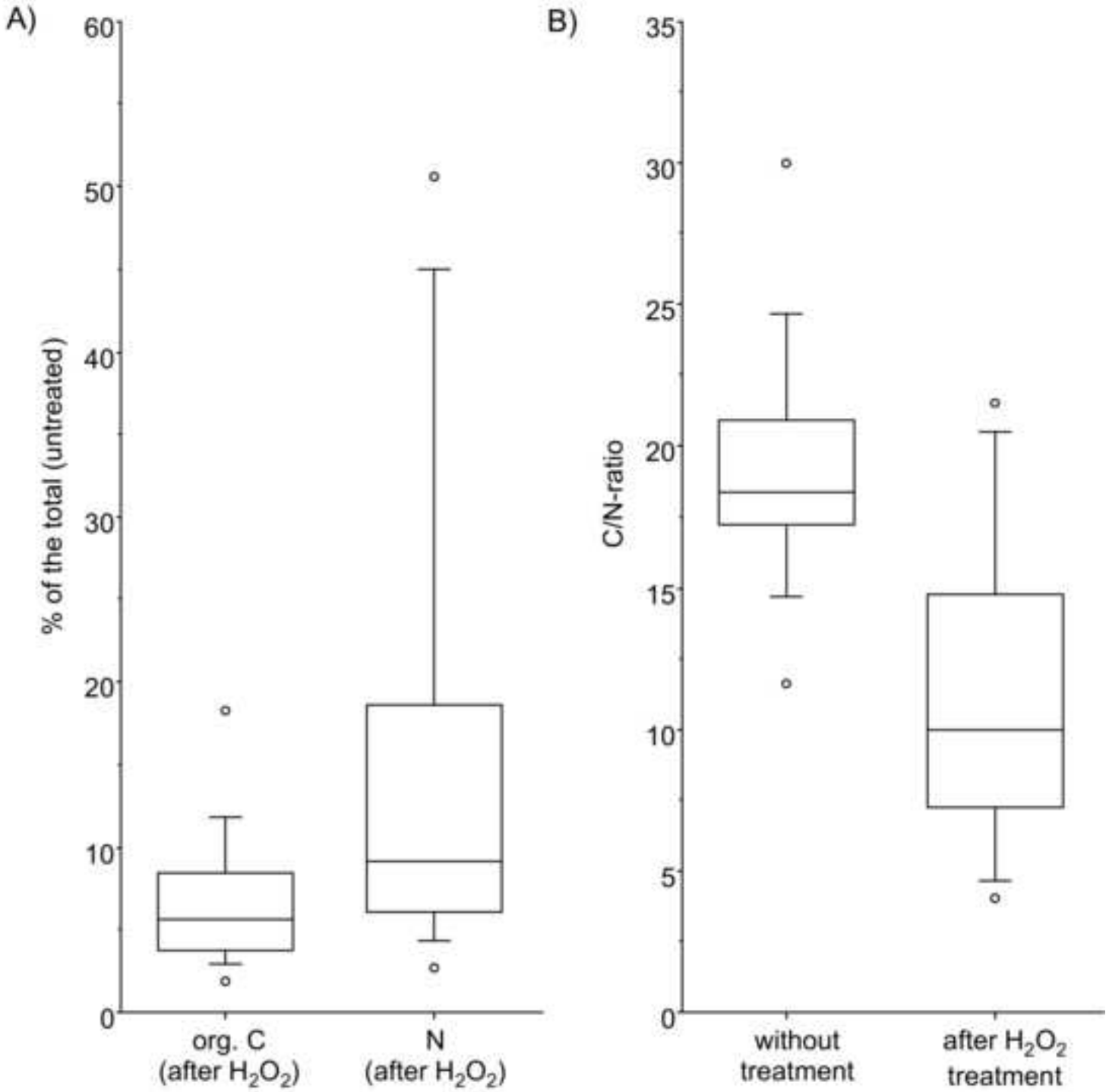

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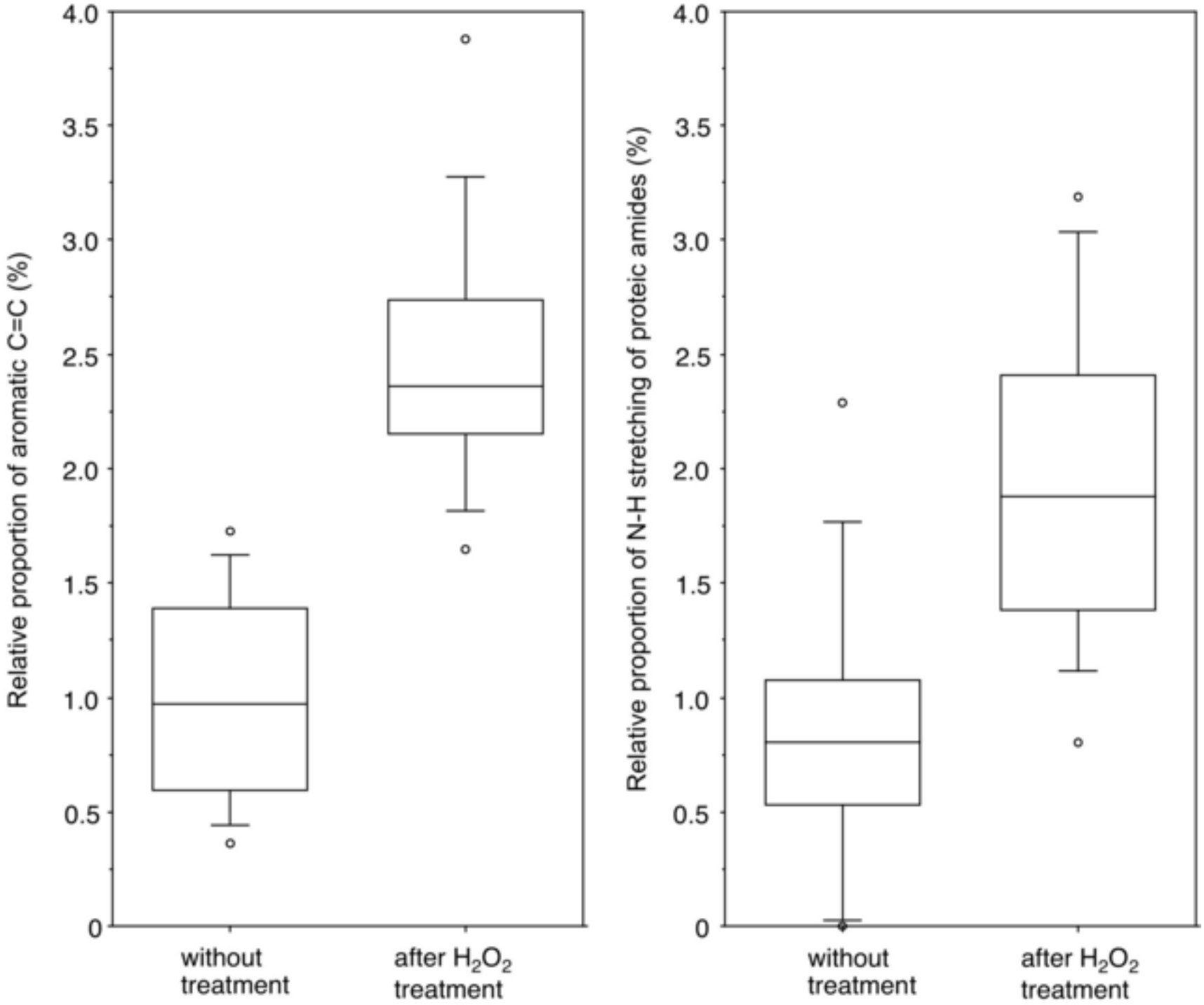

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